Chaotic Reaction Dynamics and the Phase Space Geometry of Multi-dimensional Chemical Reaction

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How systems climb through saddles from one basin to another in a multi-dimensional phase space of reaction dynamics, or in general, how reaction dynamics evolves on rugged energy landscapes with multi-saddles is one of the most intriguing subjects over the past decade. The introduction of the concept of *transition state* by Eyring and Wigner in 1930s [1] gave us great insights in understanding the kinetics of chemical reactions. In a wide class of chemical reaction theories [1-2], it is commonly assumed the existence of a transition state, or a hypersurface, which divides the phase space into reactant and product regions, and over which a chemical reactive path crosses only once in its way of reaction. However, this *no-return* hypothesis is in general not satisfied in many reaction rate theories in which the reaction rates are usually overestimated due to the problem of local recrossings. The local recrossing problem, that is, under what circumstance a dividing hypersurface exists and how such hypersurface can be found in multi-dimensional phase space, remains one of the most challenging subjects in chemical physics.

In order to resolve this problem, several generalization of the traditional transition state theory has been proposed. These included the variational transition state theory [3], which finds the optimized dividing surface in the configurational space by minimizing the recrossings, and the generalized Langevin formulation proposed by Kramers [4], Grote and Hynes [5], which regards the recrossings as *molecular friction* arisen from the *bath* degrees of freedom resulting in retardation of the reactive trajectories. Despite their successes in estimating the reaction rates, none of these approaches can provide us a clear mechanical picture of the reaction dynamics when passing through the transition state.

Recently, one of the authors (T.K.) [6] demonstrated that, in the saddle regions of strongly coupled N-particle Hamiltonian systems, the action associated with the reactive coordinate (in phase space) tends to stay invariant even up to energies high enough for the dynamics of the bath degrees of freedom to become chaotic. It has been shown that this ***regularity*** in the saddle region has its dynamical origin in the existence of a phase space geometrical structure called ***normally hyperbolic invariant manifold*** (NHIM) [7]. For saddle points of the type saddle x center x x center, NHIM can be explicitly constructed by performing the ***Lie canonical perturbative transformation*** (LCPT) [6] to the phase space coordinates in the saddle region. In this case, the resonance condition, which usually spoils the perturbation scheme near elliptic equilibrium points due to the small denominator problem [8], can never be satisfied among pure imaginary frequency (associated with the reactive mode) and real frequencies (associated with the bath modes) for saddle points of the type saddle x center x x center. Therefore, LCPT transforms the Hamiltonian into a normal form so that the transformed action associated with the reactive coordinate is a constant of motion near the saddle point. We can then easily construct a transition state free from local recrossing in terms of the transformed coordinates (normalized coordinates).

As a result, this geometrical representation provides us a multidimensional, no-return dividing hypersurface in phase space across the saddle region. It also enables us to see in a priori when and how chemical system climbs through the saddle to the product state, or returns to its original state without reacting. This understanding should, for example, help us to control reaction

kinetics by letting us recognize what kinds of initial conditions are most likely to lead a system through a saddle. Furthermore, the network formed by the ***stable/unstable invariant manifolds*** of NHIMs together with their *homoclinic/heteroclinic intersections* with each others offers us the *skeleton* of reaction dynamics in the multi-dimensional phase space. This skeleton then provides us the road map of how reactions take place in multi-saddle and multi-basin energy landscapes.

Despite of the important role it plays in the study of reaction dynamics in terms of phase space structure, the properties of NHIMs have still not been fully understood. To our best knowledge, the LCPT carried out so far in the construction of NHIMs in the literature normalized all degrees of freedom including both the reactive and bath modes. This means that the normalized Hamiltonian is completely integrable near the saddle region. We will call such case as ***full LCPT***. One advantage of full LCPT is that the dynamics of the normalized coordinates can be solved exactly due to the integrability. However, one can easily notice that full LCPT fail to reveal the chaotic properties of NHIM since it is well known that the on-set of chaos is caused by resonance overlapping and non-integrability in Hamiltonian dynamics [8]. Therefore, in order to explore the chaotic regime of NHIM and its stable/unstable manifolds, we carry out a modified normalization procedure in our research in which only the reactive mode is normalized. This means that the normalized Hamiltonian is cyclic only in the normalized coordinates associated with the reactive mode. We call this normalization scheme as ***partial LCPT***. Since the resonance terms are kept in the bath modes, one can then investigate various chaotic properties of NHIM and its stable/unstable invariant manifolds such as the *transition to chaos* and the *breakdown of normal hyperbolicity*.

With the help of both the full and partial LCPT scheme, we are able to give an explicit visualization of the molecular dynamics associated with the phase space geometrical structures discussed above. We can also demonstrate the corresponding motions of the molecules inside the NHIM with various energies above the saddle point. In particular, we can clarify from our graphical presentation the difference between the motions corresponding to the *normal form* coordinates, which is obtained by full (or partial) LCPT and those corresponding to the *normal mode* coordinates, which is valid only in the quadratic (or harmonic) regions (i.e. by neglecting cubic or higher order terms in power of coordinate and momentum) of the potential. In order to apply our theory to realistic chemical systems, we consider the problem of HCN isomerization. Its reaction dynamics and the corresponding geometrical structures in the phase space was studied recently by Wiggins et. al. [9] using full LCPT. Their studies mainly concerned with the low-energy regime above the saddle point in which the dynamics is integrable and the effects of resonance are negligible. However in our work, we deal with a more challenging problem of extending the LCPT to the intermediate- and high-energy regime above the saddle point. In this case, partial LCPT are used to extract the nonlinear and chaotic properties of reaction dynamics from the geometrical structures in the multi-dimensional phase space.

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